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EXCIPLEX IONIC DISSOCIATION IN NON-POLAR SOLVENT  
INDUCED BY MULTIPOLAR SALT COMPLEXES(U) ILLINOIS UNIV  
AT URBANA DEPT OF CHEMISTRY B E GOODSON ET AL.

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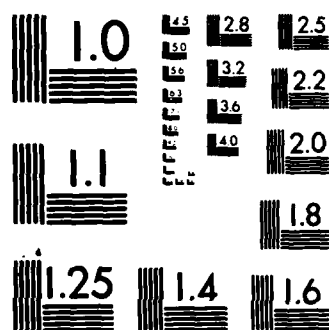
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<p>The exciplex formed from pyrene and 1,4-dicyanobenzene in chloroform solution is quenched by tetra-n-butylammonium tetrakisfluoroborate. Laser Raman analysis reveals that the salt is a more effective quencher at low concentrations than at high concentrations. Related non-linear effects are observed. The yield of radical ions formed by reaction of the salt with the exciplex is determined by laser transient absorption spectroscopy. Very little pyrene radical cation is formed at low salt concentration even though significant exciplex quenching occurs. These effects are a consequence of complex formation of the salt.</p>		

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to form a quadrupolar dimer from a dipolar monomer. The quadrupole quenches the exciplex and leads to the generation of radical ions, and the dipole quenches but does not give ions. We have demonstrated that the radical ions resulting from quadrupolar quenching are capable of undergoing characteristic chemical reactions.

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Exciplex Ionic Dissociation in Non-Polar Solvent  
Induced by Multipolar Salt Complexes

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Abstract: The exciplex formed from pyrene and 1,4-dicyanobenzene in dimethoxyethane solution is quenched by tetra-n-butylammonium tetrafluoroborate. Stern-Volmer analysis reveals that the salt is a more effective quencher at low concentrations than at high concentrations. Related non-linear effects are observed when the yield of radical ions formed by reaction of the salt with the exciplex is determined by laser transient absorption spectroscopy. Very little pyrene radical cation is formed at low salt concentration even though significant exciplex quenching occurs. These effects are a consequence of association of the salt to form a quadrupolar dimer from a dipolar monomer. The quadrupole quenches the exciplex and leads to the generation of radical ions, and the dipole quenches but does not give ions. We have demonstrated that the radical ions resulting from quadrupolar quenching are capable of undergoing characteristic chemical reactions.





Exciplex intermediates play a pervasive role in organic photochemistry.<sup>1</sup> In relatively non-polar solvents, radiative relaxation of the exciplex often occurs in competition with chemical reactions. In more polar solvents, dissociation of the exciplex to radical ions is the dominant reaction when it is permitted energetically. Salt effects are often used to control or probe organic reactions.<sup>2</sup> However, only quite recently have salts been employed in the investigation of exciplexes.<sup>3,4</sup> Herein we report the results of a study of the interactions between tetra-n-butylammonium tetrafluoroborate ( $R_4NBF_4$ ) and the exciplex formed from singlet excited pyrene and 1,4-dicyanobenzene,  $(Py-DCNB)^{*1}$  in dimethoxyethane (DME) solution. The findings reveal that  $(Py-DCNB)^{*1}$  is quenched by monomeric, dipolar  $R_4NBF_4$  without formation of ions, but that reaction of the exciplex with quadrupolar complexes  $(R_4NBF_4)_2$  leads to efficient formation of pyrene radical cation ( $Py^{\cdot+}$ ) and dicyanobenzene radical anion ( $DCNB^{\cdot-}$ ). This phenomenon is useful both for controlling the chemical reactions of exciplexes and for analyzing putative electron-transfer reactions.

The fluorescence of pyrene in DME is rapidly and irreversibly quenched by addition of DCNB, and simultaneously a new, broad emission centered at 450 nm due to  $(Py-DCNB)^{*1}$  appears in the spectrum.<sup>5</sup> The fluorescence of pyrene is unaffected by addition of  $R_4NBF_4$ , but the emission of the exciplex is quenched by this salt. In contrast to observations reported for related systems,<sup>3</sup> Stern-Volmer analysis of the exciplex quenching by the salt reveals a distinctly non-linear relationship, Figure 1.<sup>6</sup> In effect, the salt is a less effective quencher at higher concentrations than it is at the lower concentrations. Precisely the same non-linear behavior is observed when the lifetime of the exciplex is monitored.

Excitation of a DME solution of pyrene containing 0.02 M DCNB with the output of a nitrogen laser (15 ns, 337 nm, 7mJ, absorbed exclusively by the pyrene)<sup>7</sup> permits analysis of these reactions by transient absorption spectroscopy. In the absence of added salt this experiment reveals, not unexpectedly, that the radical ions are not formed from dissociation of the exciplex in this relatively non-polar solvent. However, when the solution also contains 0.05 M  $R_4NBF_4$  the absorbance of  $Py^+$  is readily detected, and its yield (determined from the absorbance change at 445 nm)<sup>8</sup> is virtually the same as that obtained from the dissociation of this exciplex in acetonitrile solution.<sup>5</sup> The yield of  $Py^+$  is dependent on the salt concentration in a curious, non-linear way, Figure 2. Very little  $Py^+$  is formed when the salt concentration is less than ca.  $5 \times 10^{-3}$  M even though this concentration is sufficient to quench the exciplex emission significantly, Figure 1. However,  $Py^+$  is easily detected at greater salt concentrations, and its yield rises steadily to the limiting value as the amount of salt increases. This finding underscores and expands the exciplex emission quenching results; at low salt concentration the exciplex is quenched but does not give  $Py^+$ , while at higher salt concentration  $Py^+$  is a major product. This non-linear behavior is readily traced to association of  $R_4NBF_4$  to quadrupolar dimers  $(R_4NBF_4)_2$ .

The association of un-ionized salts to quadrupoles in non-polar solvents is well-known.<sup>9</sup> Figure 3 shows a plot of the apparent molecular weight of  $R_4NBF_4$  (determined by vapor pressure osmometry) as its concentration increases in DME solution. The molecular weight is seen to increase monotonically over the salt concentration range where non-linear behavior is observed for the exciplex fluorescence quenching and for the yield of  $Py^+$ .

These observations are reasonably coupled and suggest that reaction of the exciplex with dipolar salt results in quenching but not in radical ion formation, and that the reaction of exciplex with quadrupolar salt gives radical ions in good yield, probably by an ion-pair exchange process. These concepts are illustrated in Scheme 1 and account both qualitatively and quantitatively for the findings if  $k_q > k_i$ .

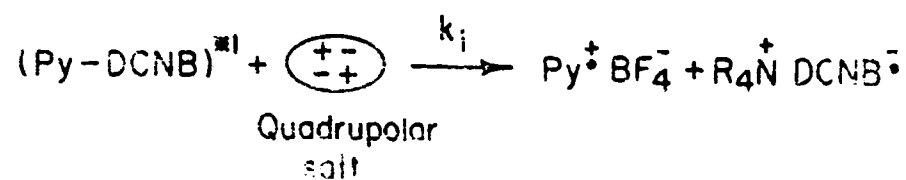
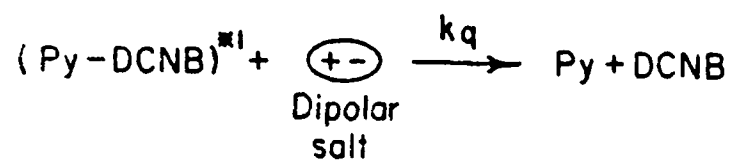
Finally, we confirmed that the radical ions formed from reaction of salt with the exciplex in non-polar solvent give the same products as those formed directly in polar solvent. The electron-transfer photooxidation of trans-stilbene sensitized by 9,10-dicyanoanthracene was used as a probe.<sup>10</sup> In acetonitrile this reaction gives benzaldehyde presumably by reaction of the stilbene radical cation with super oxide. No oxidation is observed when this reaction is attempted in DME. However, addition of 0.035 M  $R_4NBF_4$  to the DME solution leads to efficient formation of benzaldehyde.

In sum, the quenching of exciplexes by  $R_4NBF_4$  leads to ionic dissociation at high salt concentration where formation of quadrupoles occurs. At low salt concentration the exciplex is quenched but does not dissociate. This unusual behavior may be a useful probe for the intermediacy of ionic intermediates in photochemical processes.

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We thank Dr. Peter Wolynes of this Department for some thoughtful suggestions.

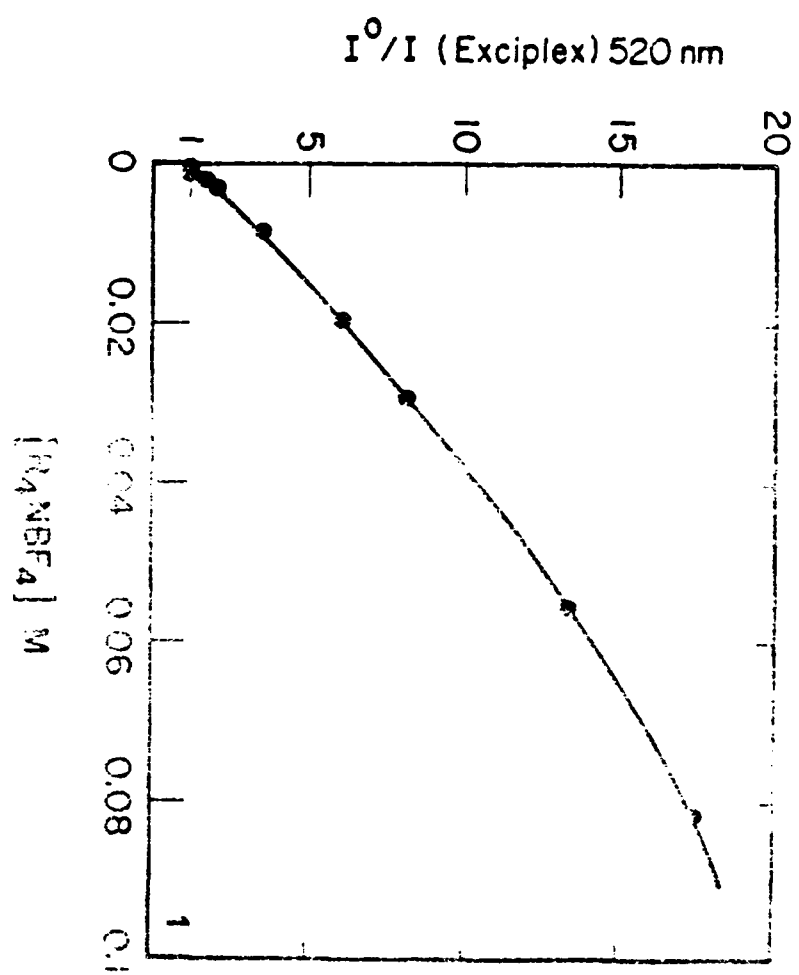
Scheme I

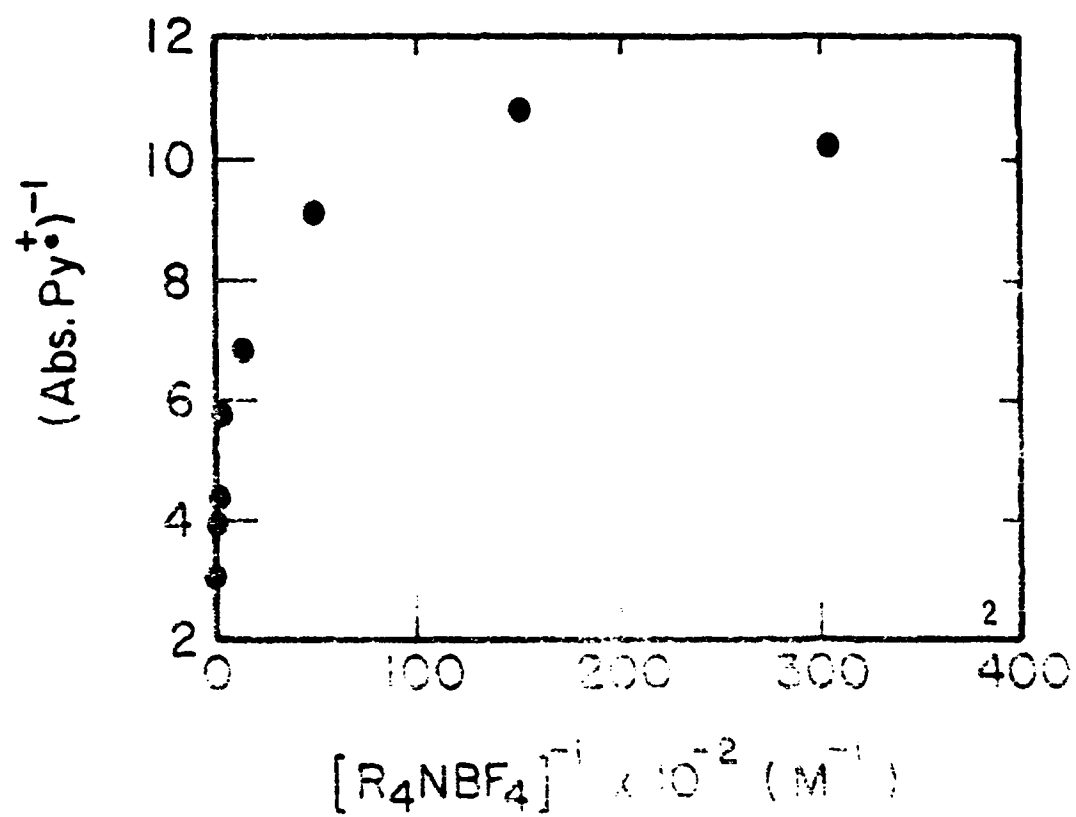


Captions for Figures

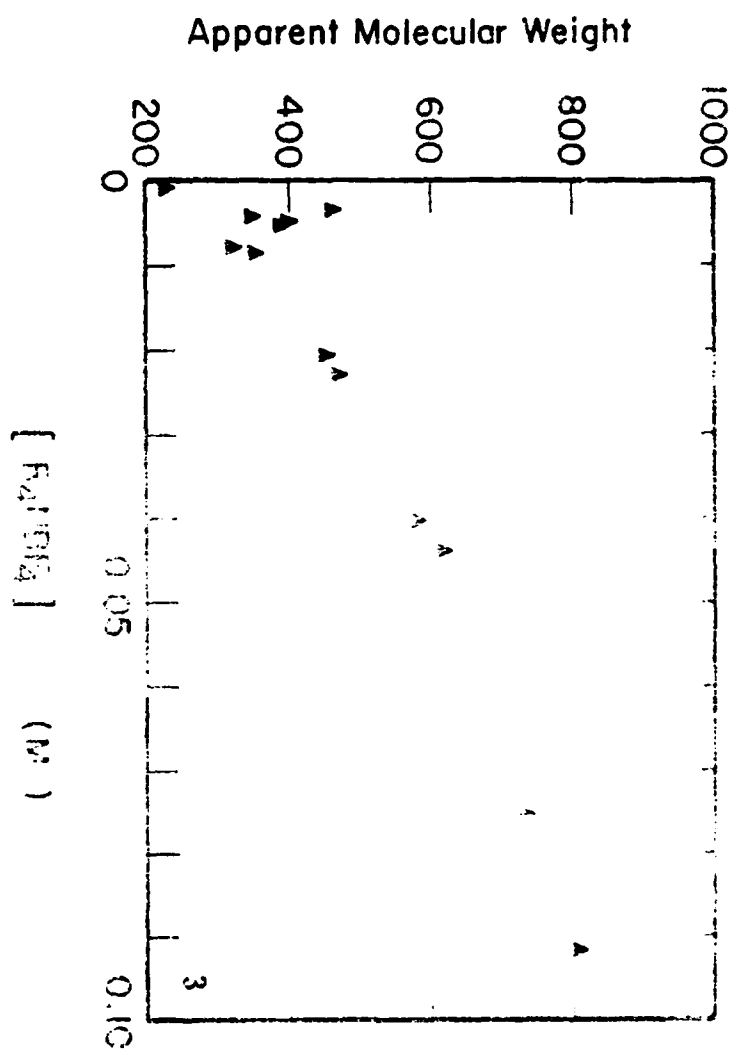
- 1) Stern-Volmer analysis of the quenching of the pyrene-dicyanobenzene exciplex in dimethoxyethane by tetra-n-butylammonium tetrafluoroborate.
- 2) Double reciprocal plot of the relative yield of pyrene radical cation against the concentration of tetra-n-butylammonium tetrafluoroborate in dimethoxyethane.
- 3) Plot of the apparent molecular weight of tetra-n-butylammonium tetrafluoroborate as a function of concentration in dimethoxyethane.

- 1) For general references on exciplexes see: Birks, J. B., "Photophysics of Aromatic Molecules" Wiley, 1970. "The Exciplex", Gordon, M.; Ware, W. R. eds., Academic Press, 1975. Masuhara, H.; Mataga, N. Acc. Chem. Res. 1981, 14, 312. Mattes, S. L.; Farid, S. Acc. Chem. Res. 1982, 15, 80-86. Davidson, R. S. Adv. Phys. Org. Chem. 1983, 19, 43.
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- 3) Kitamura, N.; Imabayashi, S.-i.; Tazuke, S. Chem. Lett. 1983, 455.
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- 5) Grellman, K. H.; Watkins, A. R.; Weller, A. J. Chem. Phys. 1972, 76, 469.
- 6) Similar observations have been made by R. Hartley and L. Faulkner (R. Hartley, Ph.D. Thesis, University of Illinois 1984) for pyrene-dimethyl-aniline exciplexes, and we have seen identical behavior for pyrene-diethylaniline exciplexes. We thank Drs. Hartley and Faulkner for sharing their findings with us before publication.
- 7) The laser system has been described previously: Horn, K. A.; Schuster, G. B. Tetrahedron 1982, 38, 1095.
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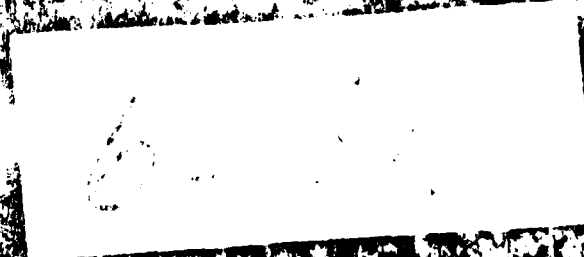






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